

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶ :**C09D 11/00****A1**

(11) International Publication Number:

WO 97/31071

(43) International Publication Date:

28 August 1997 (28.08.97)

(21) International Application Number: PCT/GB97/00449

(22) International Filing Date: 18 February 1997 (18.02.97)

(30) Priority Data:

9603667.8

21 February 1996 (21.02.96)

GB

(71) Applicant (for all designated States except US): COATES BROTHERS PLC [GB/GB]; Cray Avenue, St. Mary Cray, Orpington, Kent BR5 3PP (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): CAIGER, Nigel, Antony [GB/GB]; 4 East Side, Hurst Batch, Wookey Hole, Wells, Somerset BA5 1BE (GB). SELMAN, Hartley, David [GB/GB]; Wayside Cottage, 562 Bath Road, Saltford, Bristol BS18 3JN (GB).

(74) Agent: WALDREN, Robin, Michael; Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: RADIATION CURABLE INK COMPOSITION

(57) Abstract

A UV-curable ink jet composition comprises a polyfunctional alkoxyated or polyalkoxyated acrylate monomer (80 % to 95 % by weight), a photoinitiator (e.g. from 1 to 15 % by weight) and preferably a colourant (e.g. 1 % to 10 % by weight).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

RADIATION CURABLE INK COMPOSITION

The present invention relates to a radiation-curable ink jet composition.

Ink jet printing is well suited to applications such as short-run label printing. The inks used for this process are of generally low viscosity and are based on organic or aqueous solvent systems. In either case, the solvent content is relatively high.

When high levels of organic solvents are employed, evaporation of such solvents in the drying process potentially presents both environmental and health and safety hazards.

On the other hand, aqueous-based systems also present problems. It is relatively difficult to drive-off the water in the drying process. Such aqueous systems also tend to have a poor affinity for non-absorbent surfaces.

One potential solution to these problems, particularly in relation to the solvent base, is to use hot melt inks. However, the durability of the resultant coatings is inadequate for various applications.

The applicants have conjectured that a better solution to the foregoing problems would be to utilise an ink jet process using an ink which is UV-curable.

In another context, it is relevant to note that it is common to print direct onto polyethylene or PET bottles by means of silk-screen printing as a less expensive alternative to labelling. However, this technique results in a lower print quality than can be achieved with conventional printing on a paper label. Thus, there is a need for a high quality printing process capable of printing direct onto curved polymer substrates, with a fast drying time.

One process which potentially also lends itself to solving this objective is ink-jet printing using an ink which is radiation-curable, for example UV-curable.

It is usual to formulate UV-curable inks using a monomeric or oligomeric base vehicle. However, such polymer materials do not give the low viscosity required for a UV-curable ink-jet ink suitable for the aforementioned application, without the use of organic solvents. Although polymerisable monomers are in principle better-suited to achieving low viscosity, it is a problem to find a suitable monomer which would have sufficiently low toxicity and high thermal stability yet which gives a sufficiently flexible and durable film upon curing.

This problem has now been solved in accordance with the present invention by formulating a UV ink which contains an alkoxyated or polyalkoxyated acrylate monomer, a photoinitiator and a colourant.

A UV-curable ink-jet ink which contains a polar conductive component and a polymerisable monomer is disclosed in EP-A-0 465 039. However, this does not meet the aforementioned requirements. This ink contains the polar conductive component because it relies on so-called continuous heads which direct the ink by means of an electrostatic process. Moreover, many of the particular monomers and oligomers said to be usable in this process have serious health and safety implications. Thus, avoidance of the polar conductive material and accompanying viscosity modifiers used in the inks disclosed in EP-A-0 465 039 would be highly desirable on environmental and toxicity grounds.

Analogous non-conductive inks are disclosed in EP-A-0 540 203 which cross-references EP-A-0 465 309. Both of the latter documents envisage use of monofunctional and polyfunctional acrylate monomers. Ethoxylated monofunctional and trifunctional (but not difunctional) materials are recited. These documents also teach that the inks may optionally contain up to 70% by weight of difunctional material and optionally up to 10% by weight of trifunctional material.

Another monomer-based composition is described in US-A-4 303 924 but this is said to require application in an inert atmosphere.

UV-curable photoresists for printed circuit board applications and which contain low levels of ethoxylated acrylate monomers are disclosed in US-A-5 270 368.

Thus, there remains a need for a low viscosity radiation-curable ink jet composition with low toxicity and/or irritancy and which produces high quality print.

A new form of ink has now been devised which overcomes the various aforementioned problems and meets the aforementioned objectives. Thus, one aspect of the present invention provides a radiation-curable ink jet composition comprising, from 80% to 95% by weight of polyfunctional alkoxyated and/or polyfunctional polyalkoxyated acrylate monomer material; and a photoinitiator

The amounts of the acrylate monomer, photoinitiator, and colourant will vary according to the particular equipment and application. However, typically, the amount of photoinitiator is from 1% to 15% by weight of the total composition.

The polyfunctional alkoxyated or polyalkoxyated acrylic monomer material preferably comprises one or more di- or tri-acrylates. However, alkoxyated or polyalkoxyated acrylic monomers of higher functionality may also be used alone or together with one or more di- and/or trifunctional materials. The only requirement is that the total amount of the polyfunctional material (alkoxyated + polyalkoxyated) is in the range of from 80% to 95% by weight of the total composition. Preferably, the number of alkoxy groups is from 1 to 20 per molecule of the monomer. Also preferably, the or each alkyleneoxy group is a C₂-C₄ alkyleneoxy. Most preferred are ethoxy (EO) or propoxy (PO) groups.

Suitable polyfunctional alkoxyated or polyalkoxyated acrylates may be selected from alkoxyated, preferably ethoxyated or propoxyated, variants of the following: neopentyl glycol diacrylates, butanediol diacrylates, trimethylpropane tri-acrylates and glyceryl triacrylate.

Optionally, compositions according to the invention may also contain some monofunctional alkoxyated or polyalkoxyated acrylated monomer material, for example at up to 10% by weight of the total composition, e.g. selected from one or more of alkoxyated, e.g. ethoxyated or propoxyated, variants of the following: tetrahydrofurfuryl acrylates, cyclohexyl acrylates, alkyl acrylates, nonyl-phenol acrylate and polyethylene or polypropylene glycol acrylates.

Optionally, compositions according to the present invention may also comprise minor amounts of non-alkoxyated radiation curable monomer material, either monofunctional or polyfunctional, preferably up to no more than 5% by weight of the total composition, e.g. selected from one or more of octyl acrylate, decyl acrylate, N-vinylpyrrolidone, ethyl diglycol acrylate, isobornyl acrylate, ethyl-hexyl acrylate, lauryl acrylate, butanediol monoacrylate, β -carboxyethyl acrylate, isobutyl acrylate, polypropylene glycol monomethacrylate, 2-hydroxyethyl methacrylate, difunctional (meth)acrylic acid esters, e.g. hexanediol di-(meth)acrylate, tetraethylene glycol diacrylate, tripropylene glycol diacrylate, butanediol diacrylate, polyethylene glycol diacrylates and triethylene glycol dimethacrylate. However, most preferably such non-alkoxyated monomer materials are omitted altogether.

A wide spectrum of photoinitiators are commercially available and a non-exhaustive selection of appropriate types include xanthone or thioxanthone types, benzophenone types, quinone types and phosphine oxide types. Sometimes, it is also desirable to include, as well as a primary photoinitiator, a co-initiator should also be included, most preferably of the amine or aminobenzoate type. In that case, it is preferred for the total photoinitiator (primary initiator plus co-initiator) to be within the aforementioned preferred range. For example, typical co-initiators are aminobenzoate and acrylated amine co-initiators, these generally being used with the xanthone/thioxanthone types of primary photoinitiator.

In its broadest sense, the present invention provides a radiation curable ink jet composition. That is to say, a composition which is curable by application of suitable radiation such as ultra-violet (UV) radiation or electron-beam radiation. Such a composition may be only a substantially colourless curable varnish or a substantially colourless radiation-curable base to which a colourant may be added. In the context of the present invention, the term colourant covers both materials which endow an actual visual colour and/or another optical property such as fluorescence. Colourants are typically

included in amounts of from 1% to 10% of total colourant(s) by weight of the total composition.

Broadly speaking, colourants may be considered as falling into two classes, namely dyes, which are substantially soluble in the ink composition, and pigments, which are dispersed in the ink composition in the form of fine particles, if necessary with the aid of a suitable dispersant. Pigments may be selected from a wide range of classes, for example, Pigment Red 57:1, Pigment Red 52:2, Pigment Red 48:2, Pigment Blue 15:3, Pigment Green 7, Pigment Yellow 83, Pigment Yellow 13, Pigment White 6, Pigment Black 7. A non-exhaustive list of examples of such pigments include the following from the Irgalite range ex CIBA: Rubine L4, Bordeaux CM, Red 2BP, Blue LG, Green GLN, Yellow B3R and yellow LBG; as well as Tioxide RHD6 (ex Tioxide) and Special Black 250 (ex Degussa).

Ink compositions according to the present invention optionally may also comprise one or more minor ingredients, for example, surfactants, levelling additives, photoinitiator stabilisers, wetting agents and pigment stabilisers. The latter may for example be of polyester, polyurethane or polyacrylate types, especially in the form of high molecular weight block co-polymers, and would typically be incorporated at from 2.5% to 100% by weight of the pigment. Suitable examples are Disperbyk 161 or 162 (ex BYK Chemie) or Solsperse ex Zeneca. Suitable photoinitiator stabilisers include those disclosed in EP-A-0 465 039.

Suitable surfactants are preferably of non-ionic type, for example Fluorad FC430 (ex 3M Corp.). Such surfactants (when present) are preferably included in an amount of 0.1% to 10% by weight of the total composition.

Compositions according to the present invention are preferably substantially free or totally free of organic solvent. Thus, they preferably contain less than 10%, more preferably less than 5%, especially less than 1% and most preferably less than 0.1% of organic solvent(s) as expressed by weight of the total composition.

The invention will now be explained in more detail by way of the following non-limiting examples, in which all amounts expressed as percentages are percentages by weight of the total composition. All percentages herein, likewise represent percentages by weight of the total composition, unless it is explicitly specified otherwise.

EXAMPLE 1

Isobornyl acrylate	50.0
Ethoxylated trimethylol propane triacrylate	27.5
Propoxylated neopentyl glycol diacrylate	15.0
Pigment blue 15:3	3.0
High molecular weight hyperdispersant	0.5
2-ethyl anthraquinone (photoinitiator)	3.7
Fluoro surfactant	<u>0.3</u>
	100%

EXAMPLE 2

Ethoxylated neopentyl glycol diacrylate	93.0
Pigment black 7	2.5
High molecular weight block co-polymer dispersant	0.5
2-ethyl anthraquinone (photoinitiator)	3.7
Fluoro surfactant	<u>0.3</u>
	100%

EXAMPLE 3

Ethoxylated trimethylol propane triacrylate	28.0
Isobornyl acrylate	64.7
Pigment black 7	2.5
High molecular weight block co-polymer dispersant	0.5
Isopropyl thioxanthone (photoinitiator)	1.0
2-benzyl-2-dimethylamine-1-(4 morpholinopheny) butan-1-one (photoinitiator)	0.5
4-phenyl ibenzophenone (photoinitiator)	1.0
(2-ethyl)hexyl 4-dimethylamino benzoate (co-initiator/synergist)	1.5
Fluoro surfactant	<u>0.3</u>
	100%

EXAMPLE 4

Polyethylene glycol diacrylate	5.2
2(2-ethoxyethoxy)ethylacrylate	50.2
Ethoxylated trimethylol propane triacrylate	30.0
Pigment black 7	2.5
High molecular weight block co-polymer dispersant	0.5
Acrylated amino co-initiator	7.0
Isopropyl thioxanthone (photoinitiator)	2.5
2-benzyl-2-dimethylamine-1-(4 morpholinopheny) butan-1-one (photoinitiator)	1.0
4-phenyl ibenzophenone (photoinitiator)	1.0
Fluoro surfactant	<u>0.3</u>
	100%

EXAMPLE 5

Isobornyl acrylate	40.0
2(2-ethoxyethoxy) ethylacrylate	20.0
Propoxylated neopentyl glycol diacrylate	10.0
Ethoxylated trimethylol propane triacrylate	22.5
Pigment red 48:2	3.0
High molecular weight block co-polymer dispersant	0.5
2-ethyl anthraquinone (photoinitiator)	3.7
Fluoro surfactant	<u>0.3</u>
	100%

In the light of these Examples, modifications of such Examples, as well as other Examples, all within the scope of the invention as defined by the appended claims, will now be apparent to persons skilled in this art.

CLAIMS:

1. A radiation-curable ink jet composition comprising:-
from 80% to 95% by weight of polyfunctional alkoxylated and/or polyfunctional polyalkoxylated acrylate monomer material; and
a photoinitiator.
2. A composition according to claim 1, comprising from 1% to 10% by weight of the photoinitiator.
3. A composition according to either preceding claim, further comprising a colourant.
4. A composition according to claim 3, comprising from 1% to 10% by weight of the colourant.
5. A composition according to claim 3 or claim 4, wherein the colourant comprises a pigment.
6. A composition according to any preceding claim, wherein the acrylate monomer comprises a di- or tri-acrylate.
7. A composition according to any preceding claim, wherein the acrylate monomer comprises an ethoxylated, polyethoxylated, propoxylated and/or polypropoxylated material.
8. A composition according to any preceding claim, further comprising a co-photoinitiator.
9. A composition according to claim 8, wherein the co-photoinitiator comprises an amine or amino-benzoate co-photoinitiator.
10. A composition according to any preceding claim, further comprising a surfactant.
11. A composition according to claim 10, comprising from 0.1% to 10% by weight of the surfactant.

12. A composition according to claim 10 or claim 11, wherein the surfactant comprises a nonionic surfactant.
13. A composition according to any preceding claim, comprising less than 10%, preferably less than 5%, more preferably less than 1% and especially less than 0.1% of total organic solvent by weight of the total composition.
14. A method of ink jet printing using a printer provided with piezoelectric print heads and an ink having a composition according to any preceding claim.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 97/00449

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 270 368 A (LENT BRUCE A ET AL) 14 December 1993 cited in the application ---	1
A	EP 0 540 203 A (DOMINO PRINTING SCIENCES PLC) 5 May 1993 cited in the application see abstract ---	1-14
A	EP 0 465 039 A (DOMINO PRINTING SCIENCES PLC) 8 January 1992 cited in the application see abstract ---	1-14
A	US 4 303 924 A (YOUNG JR AINSLIE T) 1 December 1981 cited in the application see abstract ---	1-14
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

20 May 1997

Date of mailing of the international search report

- 6. 06. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Miller, A

INTERNATIONAL SEARCH REPORT

Int Application No
PCT/GB 97/00449

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 95 11219 A (PERSTORP AB ;SOERENSEN KENT (SE)) 27 April 1995 see abstract see page 8, paragraph 5 -----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/00449

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5270368 A	14-12-93	NONE	
EP 0540203 A	05-05-93	DE 69215835 D	23-01-97
		DE 69215835 T	03-04-97
		JP 5214280 A	24-08-93
		US 5275646 A	04-01-94
EP 0465039 A	08-01-92	DE 69106952 D	09-03-95
		DE 69106952 T	24-05-95
		JP 5214279 A	24-08-93
		US 5275646 A	04-01-94
US 4303924 A	01-12-81	NONE	
WO 9511219 A	27-04-95	AU 8007994 A	08-05-95